National Institute of Standards & Technology

Certificate of Analysis

Standard Reference Material® 2683b

Sulfur and Mercury in Coal

This Standard Reference Material (SRM) is intended primarily for use in the evaluation of techniques employed in the determination of sulfur, mercury, and ash content, in coal and materials of a similar matrix. SRM 2683b consists of 50 g of bituminous coal ground to pass a 250 µm (60 mesh) sieve, homogenized, and packaged in an amber glass bottle under an argon atmosphere.

Certified Values: The certified values for sulfur and mercury, expressed as mass fractions [1] on a dry basis, (see Drying Instructions) are provided in Table 1. The certified values are based on or directly traceable to a single NIST primary method. A NIST certified value is a value for which NIST has the highest confidence in its accuracy in that all known or suspected sources of bias have been investigated or accounted for by NIST.

Reference Value: The reference value for ash content [2,3] is provided in Table 2. The reference value is based on data from laboratories participating in an interlaboratory study done in conjunction with the Canada Centre for Mineral and Energy Technology (CANMET) Service Program for the Evaluation of Codes and Standards (CANSPECS) in June 1997 (CANSPECS No. 52). A reference value is a non-certified value that is the best estimate of the true value; however, the value does not meet NIST criteria for certification and is provided with an associated uncertainty that may reflect only measurement precision and may not include all sources of uncertainty.

Information Values: Information values based on the CANSPECS 52 Coal Round Robin study, expressed as mass fractions on a dry basis, are provided in Table 3. These are non-certified values with no uncertainty assessed that are provided for information purposes only. In addition, summary data from the CANMET CANSPECS 52 Coal Round Robin are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to more fully characterize the matrix. The CANMET CANSPECS results were not used in calculating the certified values for sulfur and mercury and should **NOT** be used as substitutes for NIST values.

Expiration of Certification: The certification of SRM 2683b is valid, within the measurement uncertainties specified, until **31 December 2010**, provided the SRM is handled in accordance with the instructions given in this certificate (see Instructions for Use). This certification is nullified if the SRM is contaminated or otherwise modified in a manner other than as intended.

Maintenance of SRM Certification: NIST will monitor representative samples of this SRM over the period of its certification. If substantive changes occur that affect the certification before the expiration of this certificate, NIST will notify the purchaser. Return of the attached registration card will facilitate notification.

The coordination of the technical measurements leading to certification was performed by G.C. Turk of the NIST Analytical Chemistry Division.

The technical and support aspects involved in the preparation, certification, and issuance of this SRM were coordinated through the NIST Standard Reference Materials Program by B.S. MacDonald.

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Certificate Issue Date: 23 January 2001
See Certificate Revision History on Last Page

Nancy M. Trahey, Chief
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Certification analyses for sulfur were performed by W.R. Kelly, T.L. Quinn, and R.D. Vocke of the NIST Analytical Chemistry Division. Certification analyses for mercury were performed by S.L. Long and W.R. Kelly of the NIST Analytical Chemistry Division. Moisture analyses were preformed by J.L. Mann and W.R. Kelly of the NIST Analytical Chemistry Division.

Homogeneity testing of the bulk material by X-ray fluorescence was performed by A.F. Marlow of the NIST Analytical Chemistry Division.

Statistical analyses leading to the certified and reference values were performed by W.F. Guthrie of the NIST Statistical Engineering Division.

INSTRUCTIONS FOR USE

Sampling: The unit should be thoroughly mixed by rotating the bottle before sampling. A minimum sample mass of 150 mg should be used for analytical determinations to be related to the sulfur and mercury values provided. The ash content was determined using a nominal sample mass of 1 g. The SRM should be stored in its original bottle, tightly sealed and away from sunlight and intense sources of radiation.

Drying Instructions: In order for users to directly relate their measurements to the certified and reference values, drying corrections should be measured and applied at the time of the analysis. The correction for sulfur and/or ash analysis is determined by drying separate 1 g samples in a nitrogen atmosphere at 105 °C to a constant mass [3] or equivalent technique. During drying at NIST, the mass loss of SRM 2683b samples were observed to stabilize after approximately 50 minutes. The average mass loss measured at NIST for SRM 2683b was 3.86 % ± 0.03 %.

At NIST, a study was also conducted to quantify the difference between drying in air and nitrogen atmospheres. The average weight loss determined at NIST for SRM 2683b dried in air was 3.65 % ± 0.03 %.

PREPARATION, HOMOGENEITY TESTING, AND ANALYSIS[1]

Preparation: SRM 2683b is a 50/50 blend of Illinois State Geological Survey IBC-112 coal, (Herrin, Illinois No. 6 coal) and Electric Fuels Corporation SPC-B Coal, (a blend of various coal seams found in Harlan County, KY). Each coal was crushed to a nominal 8 mesh (4.76 mm) particle size and subsequently pulverized until the entire lot passed a 60 mesh sieve (250 mm). Next, the two coals were combined and mixed into a single lot. The entire lot was then divided by the spinning riffle technique into two portions. One portion was stored in bulk under an argon atmosphere. The other portion was further divided into SRM units by the spinning riffle technique and bottled under an argon atmosphere.

Homogeneity Testing: Thirty bottles from the lot were selected for homogeneity testing. Samples from each bottle were analyzed by X-ray fluorescence for sulfur and by ASTM D 3174 for ash [2]. In each case, components of variation attributed to bottle-to-bottle variability were detected. The standard deviation of random bottle-to-bottle differences in sulfur concentration is estimated to be 0.96 % ± 0.27 % relative to the certified sulfur concentration. The standard deviation of random bottle-to-bottle differences in ash content is estimated to be 0.23 % ± 0.17 % relative to the reference value given for ash. Homogeneity estimates for both constituents are 95 % confidence intervals.

Analysis: The certified value for sulfur is based on measurements by isotope dilution thermal ionization mass spectrometry, (ID-TIMS) [4]. The certified value for mercury is based on measurements by isotope dilution cold vapor inductively coupled mass spectrometry (ID-CV-ICP- MS) [5].

[1]Certain commercial equipment, instrumentation, or materials are identified in this certificate to specify adequately the experimental procedure. Such identification does not imply recommendation or endorsement by the NIST, nor does it imply that the materials or equipment identified are necessarily the best available for the purpose.

Table 1. Certified Values (dry basis)

Elements	Mass Fraction
Sulfur	1.955 % ± 0.041 %
Mercury	90.0 µg/kg ± 3.6 µg/kg

The uncertainty in each certified value is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [6]. The quantity u_c represents, at the level of one standard deviation, the combined effect of uncertainty due to components associated with material in homogeneity and measurement variability. The quantity, k, is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. The observed variation of results was greater than expected for each analytical technique used. Therefore, a prediction interval was used to account for the variability in this material [7]. For sulfur the coverage factor, k = 2.035, is determined from the Student's t-distribution with 31 degrees of freedom and a confidence level of 95 %. For mercury the coverage factor, k = 2.424, is determined from the Student's t-distribution with 6.24 degrees of freedom and a confidence level of 95 %.

Reference Value and Uncertainty: The reference value for ash content is based on data obtained from 62 laboratories using method ASTM methods [2,3] in the CANMET CANSPECS Coal 52 Round Robin. Dry ash data from the study were corrected for moisture content based on samples dried in either air or nitrogen atmospheres. All ash values were converted to a dried in nitrogen atmosphere basis based on a drying study conducted at NIST.

Table 2. Reference Value (dry basis)

Ash Content	9.93 % ± 0.08 %

The uncertainty in the reference value for ash content is expressed as an expanded uncertainty, $U = ku_c$, calculated according to the methods in the ISO Guide [6]. A prediction interval was used to account for the variability in this material [7]. The quantity u_c represents, at the level of one standard deviation, the potential combined effects of within laboratory measurement uncertainty, between laboratory uncertainty, material inhomogeneity, and the uncertainty in the conversion of samples dried in air to a nitrogen basis. The quantity k is the coverage factor used to obtain an expanded uncertainty with an approximate confidence level of 95 %. For ash content, the coverage factor, k = 2.013, is determined from the Student's t-distribution with 46 degrees of freedom and a confidence level of 95 %.

Supplemental Information: The information values given in Table 3 are from the CANSPECS 52 Coal Round Robin study. These values are not certified and are given as additional information on the matrix.

Table 3. Information Values (dry basis)

Chlorine	1125 mg/kg
Pyritic Sulfur	0.71 %
Sulphate Sulfur	0.08 %
Gross Calorific Value	30.62 $MJ \cdot kg^{-1}$ (13163 $Btu \cdot lb^{-1}$)
Volatile Matter	36.31 %

REFERENCES

[1] Taylor, B.N., "Guide for the Use of the International System of Units (SI)," NIST Special Publication 811, 1995 Ed., (April 1995).

[2] ASTM D 3174-93, "Test Method for Ash in the Analysis Sample of Coal and Coke from Coal," **05.05** ASTM Book of Standards, West Conshohocken, PA.

[3] ASTM D 5142-90, "Standard Test Methods for Proximate Analysis of the Analysis Sample of Coal and Coke by Instrumental Procedures," **05.05** ASTM Book of Standards, West Conshohocken, PA.

[4] Kelly, W.R., Paulsen, P.J., Murphy, K.E., Vocke, R.D., and Chen, L.-T., "Determination of Sulfur in Fossil Fuels by Isotope Dilution Thermal Ionization Mass Spectrometry," Anal. Chem., **66**, p. 2505, (1994).

[5] Long, S.E. and Kelly, W.R., "Determination of Mercury in Coal Reference Materials by Isotope Dilution, Cold-Vapor ICP-MS," Fresenius Journal of Analytical Chemistry (BERM), Submitted for Publication, (September 2000).

[6] *Guide to the Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed. ISO, Geneva, Switzerland, (1993); see also Taylor, B.N. and Kuyatt, C.E., "Guidelines for Evaluating and Expressing the Uncertainty of NIST Measurement Results," NIST Technical Note 1297, U.S. Government Printing Office, Washington DC, (1994); available at http://physics.nist.gov/Pubs/.

[7] Hahn, G.J. and Meeker, W.Q., "Statistical Intervals: A Guide for Practitioners," John Wiley & Sons, Inc., NY, (1991).

Certificate Revision Date History: 23 January 2001 (Certified value for mercury and addendum with CANMET 52 Round Robin Data added); 27 October 1997 (original version).

Users of this SRM should ensure that the certificate in their possession is current. This can be accomplished by contacting the SRM Program at: Telephone (301) 975-677; Fax (301) 926-4751, E-mail srminfo@nist.gov, or via the Internet http://www.nist.gov/srm.

Addendum

Standard Reference Material® 2683b

Sulfur and Mercury in Coal

CANSPECS 52 Coal Round Robin Results: SRM 2683b was included as an unknown in the June 1997 CANSPECS 52 Coal Round Robin. Summary statistics reported by CANSPECS are provided in the addendum to this certificate to demonstrate user experience with this material using conventional methods and to better characterize the matrix. The CANSPECS 52 Coal Round Robin results should **NOT** be used as a substitute for the NIST values.

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Issue Date: 23 January 2001

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Summary of Analysis Reported by CANSPECS

CANSPECS 52 Coal Sample NIST SRM 2683b

Parameter	Consensus Value	ASTM Method Referenced for Reproducibility and Repeatability	ASTM Reproducibility Standard Deviation	CANSPECS Reproducibility Standard Deviation	ASTM Repeatability Standard Deviation	CANSPECS Repeatability Standard Deviation	Number of Labs	Number of Methods
Moisture wt %	3.62	ASTM D 3173	0.11	0.18	0.07	0.05	79	22
Ash wt % db	9.90	ASTM D 3174	0.18	0.08	0.11	0.05	79	22
Volatiles wt % db	36.31	ASTM D 3175	0.35	0.86	0.18	0.16	62	17
BTU/lb db	13163	ASTM D 5865	44	63	18	18	79	16
Carbon wt % db	73.92	ASTM D 5373	0.89	0.72	0.23	0.17	36	14
Hydrogen wt % db	4.91	ASTM D 5373	0.11	0.17	0.06	0.04	34	13
Nitrogen wt % db	1.61	ASTM D 5373	0.06	0.10	0.04	0.04	35	13
Sulfur w % db	1.94	ASTM D 4239c	0.06	0.04	0.03	0.02	76	18
Pyritic Sulfur wt % db	0.71	ASTM D 2492	0.12	0.07	0.05	0.01	14	4
Sulfate Sulfur wt % db	0.08	ASTM D 2492	0.01	0.03	0.01	0.01	12	3
Chlorine mg/kg db	1125	ASTM D 4208	163	101	69	46	25	10
Fluorine mg/kg db	75	ASTM D 3761	5	35	5	6	12	6
Mercury mg/kg db	84	ASTM D 3684	11	17	7	11	12	8
Selenium mg/kg db	1.99	ASTM D 4606	0.25	0.49	0.18	0.09	8	7
Free Swelling Index (FSI)	3.0	ASTM D 720	0.7	1.0	0.4	0.2	31	4